A STUDY OF THE PROPERTIES OF THE GLASSY PHASE IN ALUMINA SILICA REFRACTORIES

BY

WILLIAM DANIEL FITZPATRICK

B. S., University of Illinois, 1941

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SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CERAMIC ENGINEERING IN THE GRADUATE COLLEGE OF THE UNIVERSITY OF ILLINOIS, 1950

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ACKNOWLEDGEMENT

The writer wishes to express his sincere gratitude to Professor R. K. Hursh of the Department of Ceramic Engineering for his many valuable suggestions and his guidance during the course of the investigation. Thanks are also extended to Dr. A. I. Andrews, Head of the Department of Ceramic Engineering, for his interest in the work.

For his interest and encouragement, the writer wishes to thank Professor A. W. Allen of the Ceramic Engineering Department.

Thanks are due Mr. T. A. Willmore of the Ceramic Engineering Department for the use of his sonic testing equipment.

Finally, the writer wishes to express sincere gratitude to the American Refractories Institute, and to the Edward Orton Jr. Foundation. This work was made possible through the establishment of fellowships by these organizations at the University of Illinois.

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INTRODUCTION

The properties of the glassy state have been the subject of many researches. These investigations, for the most part, have been concerned with commercial glasses. Since the compositions of the glasses occurring in refractories differ greatly from those of commercial glasses, it is probable that the relations established for the commercial glasses would not be valid for those occurring in refractories. It was the purpose of this study to determine the properties of the glassy phase occurring in alumina silica refractories and the effect of the addition of Na_2, Fe_2O_3, and SiO_2 on these properties.

The devitrification of the glassy bond and its effect on the properties of commercial bricks and of a Missouri bond clay was also studied.

EXPERIMENTAL PROCEDURE

Pellets formed from the fine fraction of Georgia kaolin by dry pressing were sintered at 1200°C. and then fired at different temperatures. The minerological development was investigated by the use of a Norelco X-ray spectromenter. Pellets fired at 1550°C. were found to consist of mullite and glass.

The mullite was separated from the glass by fuming the finely ground material which had been fired at 1550°C. with dilute hydrofluoric acid. The chemical composition of the mullite and the fired clay material was determined by wet analysis. The amount of mullite present in the fired material was determined by means of the Norelco x-ray spectrometer. The composition of the glassy phase was determined by subtracting the composition of the mullite multiplied by the percent of mullite present from the composition of the fired clay.

Synthetic batches were prepared corresponding to the composition of the glass in the fired kaolin and also with additions of Na_2O, Fe_2O_3, and SiO_2. The raw batches were fused and water quenched from a temperature approximately 50°C. above the liquidus of the mixture.

The index of refraction, true specific gravity, thermal expansion, and deformation vs. temperature relationship of the glasses were determined.

The composition of the glassy bond in Fulton plastic and in Missouri flint clay was determined in the same manner as for the Georgia kaolin. Synthetic glasses were prepared and their properties determined.

The devitrification of these synthetic glasses was studied and also the behavior of the glassy bond occurring in the fired clay materials. Samples of ground material were heated to a series of temperatures for 30 minutes and quenched in air. The samples were analyzed, using the Norelco x-ray spectrometer.

Bars of Fulton plastic clay were dry pressed, and fired at 1310°C., 1425°C., and 1500°C. Some of the bars fired at 1500°C. were given a heat treatment consisting of a lowering of the temperature to 1149°C. followed by heating to and holding at 1425°C.

The modulus of elasticity, thermal expansion, and modulus of rupture of the bars as fired and after reheating at 1149°C. for 78 hours was determined.

The thermal expansion of samples of two commercial bricks was determined. The test specimens were then reheated and the thermal expansion again determined.

DISCUSSION OF RESULTS

In the mineralogical development of Georgia kaolin during firing, the mullite content increased only slightly with higher firing temperatures. The cristobalite reached a maximum amount between 1400°C. and 1450°C., and disappeared when the clay was fired at 1550°C. for four hours. The glass content increased rapidly as the firing temperature was raised above 1450°C.

The chemical compositions of the glassy bond occurring in Georgia gaolin and in the two fire clays when fired to 1550°C. for four hours are shown:

Oxide	Glassy Bond in Fired Georgia Kaolin Percent	Glassy Bond in Fired Fulton Plastic Clay - Percent	Glassy Bond in Fired Missouri Flint Clay - Percent
Si_2O	84.50	75.09	69.00
Al_2O_3	10.41	16.50	21.65
TiO_2	4.47	2.98	3.53
Fe_2O_3	0.12	1.44	1.47
KNaO	0.61	3.76	4.35

The properties determined for these glasses were as follows:

Property	Glassy Bond in Fired Georgia Kaolin	Glassy Bond in Fired Fulton Plastic Clay	Glassy Bond in Fired Missouri Flint Clay
Linear Coeffi-cient of themal expansion 20 — 500°C.)	1.247 x 10^{-6}	2.63 x 10^{-6}	3:08 x 10^{-6}
Index of Refraction	1.488	1.497	1.504
True Specific Gravity	2.290	2.382	2.398

The glass corresponding to the glassy bond in fired Georgia kaolin began to deform under its own weight at a temperature of 2760°F., and the deformation continued rather rapidly while the furnace was held at this temperature. The deformation during heating of the glass from the fired Fulton plastic clay was more rapid and began at a lower temperature. The glass from Missouri flint clay began to deform under its own weight at a temperature of 2600°F., but the resistance to deformation was increased at higher temperatures by crysalization of mullite.

The addition of Na_2O to the base glass in the fired kaolin 1) rapidly increased the thermal expansion, 2) slightly increased the index of refraction, 3) had very slight effect on the true specific gravity, and 4) rapidly decreased the resistance to deformation.

The addition of Fe_2O_3 to the base glass 1) slowly increased the thermal expansion, 2) increased the index of refraction, 3) rapidly increased the true specific gravity, and 4) slowly decreased the resistance to deformation.

Addition of SiO_3 to the base glass composition 1) decreased the thermal expansion, 2) decreased the index of refraction, 3) decreased the true specific gravity, and 4) with small additions, decreased resistance to deformotion but with larger additions, increased this resistance.

The additive factors relating to thermal expansion for Na_2O, Fe_2O_3, and Al_2O_3 in this glass were smaller than those commonly accepted for the soda-lime-silica glasses. The factor for SiO_2 showed no appreciable difference.

The glasses formed in the firing of all three clays readily devitrified at relatively low temperatures. The products of devitrification were mullite and cristobalite.

Devitrification of the glassy bond had a very slight effect on the modulus of elasticity. Since the thermal expansion was greatly increased by the presence of the devitrified cristobalite, the resistance to thermal shock was greatly reduced by the reheating at 1149°C.

The same devitrification characteristics are found in some commercial fire brick and have significant effects on their behavior in service conditions.

VITA

William Daniel Fitzpatrick was born in Monmouth, Illinois, on July 31, 1916. He attended the elementary and high schools in Pittsfield, Illinois and graduated in 1934. He entered the University of Illinois in the fall of 1937 and received a B. S. with honor in Ceramic Engineering in 1941. He was commissioned in the U.S. Navy in the spring of 1941 and served in the American and South Pacific Theatres. He was separated from the service in 1945 and entered the Graduate College College of the University of Illinois in the fall of that year. He held a Teaching Assistantship from September, 1945 to June, 1946 and an Instructorship from September, 1946 to June, 1947. He received a M. S. degree in Ceramic Engineering in 1947. He was employed for one year with the Owens-Illinois Glass Company, resigning the position to resume study in the Graduate College of the University of Illinois in the fall of 1948. He held the American Refractories Fellowship from September, 1948 to June, 1949 and the Edward Orton Jr. Fellowship in the academic year 1949-50.

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Publication:

"Waterlining as Related to Dry Beading," Finish, August (1948) (with A. I. Andrews).